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**PROCEDURE FOR THE VULCANIZATION WITHOUT SULFUR OF AN ELASTOMER
AND SELF-VULCANIZING MIXTURES ON A BASE OF EPOXIDIZED ELASTOMERS**

[Procedimento per la Vulcanizzazione Senza Zolfo di un
Elastomero e Mescole Autovulcanizzanti a Base di Elastomeri
Epossidati]

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Abstract

Process for the vulcanization without sulfur of elastomers consisting of epoxidizing elastomer to a predetermined degree, for example, natural rubber (NR), preparing a mixture including the epoxidized elastomer, possible other elastomers and a predetermined quantity of at least one compound having the following formula:



where R is arylene, alkylene, alkenylene, substituted or not substituted, or a mixture of same and where R₁ and R₂ are indifferently a carboxylic group, an aminic group and a sulfonic group or chlorosulfonic group and is subsequently, hot and under pressure, treating the mixture thus prepared. /2

This invention relates to a process for the vulcanization of an elastomer without the use of sulfur or compounds containing sulfur. The invention more particularly relates to self-vulcanizing mixtures containing at least one elastomer that is epoxidized to a predetermined degree.

It is known that mixtures on a base of rubbers and elastomers - in general so as to generate usable products - must undergo a process of vulcanization, also referred to as

¹ Numbers in the margin indicate pagination in the foreign text.

"reticulation" during which transversal bonds are created between the various polymeric chains of the elastomers; normally, these cross-bonds are made up of points of sulfur (S) that are created by means of the addition of S in the allylic position to the double bonds of the polymeric chains, an addition that is promoted and catalyzed by suitable substances that are referred to as accelerators, which include TMTM (tetramethylthiourame disulfide) and TMDT (tetramethylthiourame disulfide). The use of some of these substances may, however, involve the formation of products that are potentially harmful to health.

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A known alternative to vulcanization with sulfur is vulcanization based on the use of peroxides; but this process is very expensive and is rather complicated to implement due to the difficulty arising from the use of peroxides.

The purpose of this invention is to provide a process for vulcanization that would be devoid of the inconveniences inherent in known processes, in particular, a process that would cost less, that would not entail risks to workers and that would minimize problems connected with controlling the vulcanization

12 temperature. The procedure can be applied to make parts of pneumatic tires and other rubber articles. Another purpose of the invention is to obtain self-vulcanizing mixtures containing at least one epoxidized elastomer, most of which would be usable

to turn out safe and nontoxic products for applications for the product, for example, a nipple for a nursing bottle, can come into contact with food and/or with the skin or with the mucosae of a living being.

The abovementioned purposes are obtained by the invention on the basis of which one can implement a procedure for the vulcanization without sulfur of elastomers, characterized in that it comprises the following phases:

- preparation of a mixture including at least one elastomer epoxidized to a predetermined degree and a predetermined quantity of at least one compound having the following formula:



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where R is arylene, alkylene, alkenylene, substituted or not substituted, or a mixture of same and where R_1 and R_2 are indifferently a carboxylic group, an aminic group and a sulfonic group or chlorosulfonic group; and

- subsequently, hot and under pressure, treating the mixture thus prepared.

The invention also relates to a self-vulcanizing mixture containing at least one elastomer that is epoxidized to a predetermined degree, characterized in that it comprises a predetermined percentage of one or several vulcanizing agents having the following formula:

R1 - R - R2

where R is arylene, alkylene, alkenylene, substituted or not substituted, or a mixture of same and where R1 and R2 are indifferently a carboxylic group, an aminic group and a sulfonic group or chlorosulfonic group.

The objection of the invention also includes a self-vulcanizing mixture containing at least one elastomer epoxidized to a predetermined degree, characterized in that it comprises a predetermined quantity of a second elastomer where the repetitive units of the polymeric chain present at least one carboxylic group.

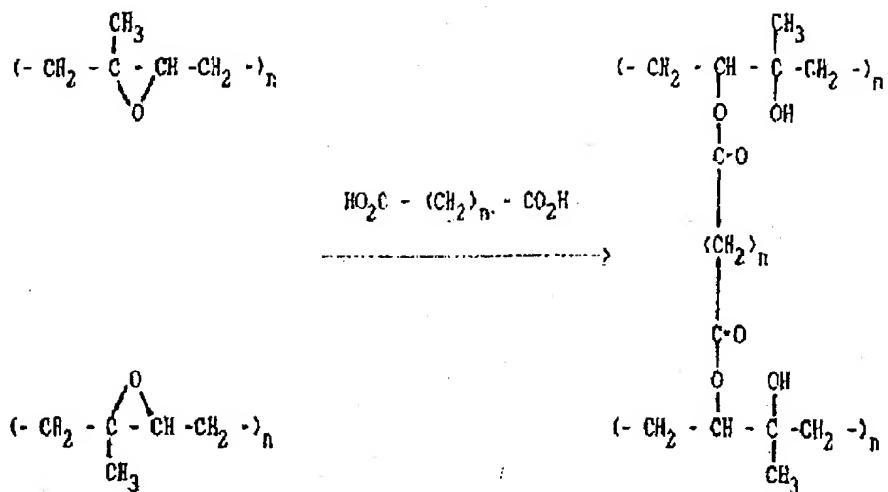
According to the preferred embodiment of the invention, we start with an already epoxidized natural rubber (ENR), that is, epoxidized to a predetermined degree of epoxidation comprised, for example, of between 25 and 50% by mole, which can be obtained under the name of EPOXYPRENE (registered trademark) /5 from MRPRA (Malaysian Rubber Producers' Research Association); to it, one adds a controlled quantity, for example, between 5 and 25-30 phr (parts by weight for every 100 parts by weight of rubber) of a vulcanizing agent consisting of an organic bicarboxylic or polycarboxylic acids or a mixture of bi- and/or polycarboxylic acids. For special uses, the addition of bi- or polycarboxylic acid can also be greater. One can use one or several of the following acids by themselves or, where possible

or opportune, mixed with each other: oxalic, malonic, succinic, glutaric, adipic, sebacic, maleic, fumaric, phthalic, isophthalic, terephthalic, citric. In particular, it turned out advisable to use, in combination with the bicarboxylic acid that is more suitable for a specific application, another bicarboxylic acid having a high pK_a , in the range between 0.5 and 5.5, for example, fumaric acid that works as an accelerator.

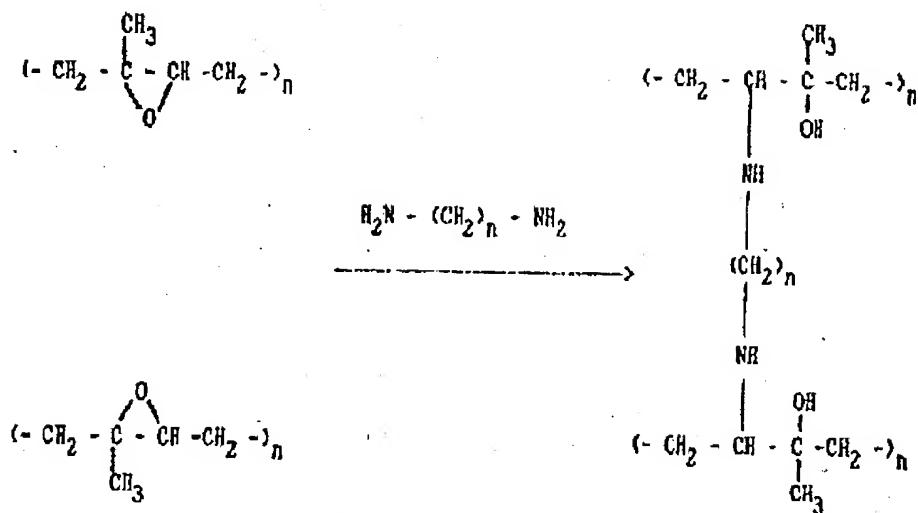
According to the invention, in addition the bi- or polycarboxylic acids, one can also use as vulcanizing agents, in combination with an elastomer having a predetermined degree epoxidation, also thiamines, for example, hexamethylenediamine, or compounds having a molecule presenting at least two sulfonic or chlorosulfonic groups or also compounds having a molecule comprising, in combination, at least one carboxylic group with an aminic group and/or sulfonic or chlorosulfonic group or, furthermore, at least one aminic group and one sulfonic or chlorosulfonic group. All of these groups, as a matter of fact, are capable of opening the epoxidic ring, thus facilitating the transversal addition of the vulcanizing agent upon two polymeric chains of adjacent elastomers according to the following formulas:

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(A) - Addition by means of carboxylic groups

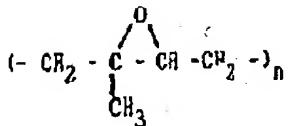
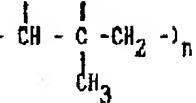
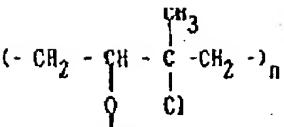
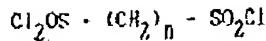
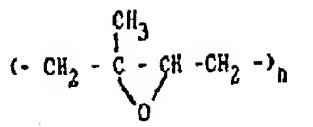


(B) - Addition by means of aminic groups



(C) - Addition by means of sulfonic groups

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The vulcanization procedure according to the invention is therefore characterized in that one prepares a mixture on a base of epoxidized elastomers and in which one uses as vulcanizing agents one or several compounds (separately or mixed with each other) in accordance with the following general formula:

(1) $\text{R}_1 - \text{R} - \text{R}_2$

where R is arylene, alkylene, alkenylene, substituted or not substituted, or a mixture of same and where R_1 and R_2 are indifferently a carboxylic group, an aminic group and a sulfonic group or chlorosulfonic group.

Next, this mixture, usually prior to forming or with possible link to auxiliary elements such as plies [warps] and the like, is subjected once the final product has been obtained with it to the action of heat and pressure according to the well-known vulcanization techniques that are normally used in vulcanization with sulfur so as to obtain the complete reaction

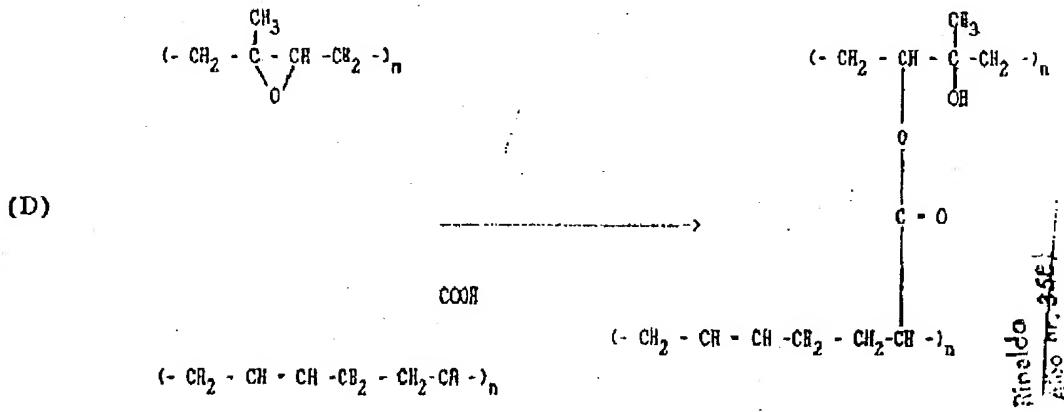
of the functional R1 and R2 groups of the vulcanizing agent upon the epoxidic rings of the elastomer. For example, this vulcanization phase involves keeping the mixture under pressure at a temperature of between 130 and 180°C for 20-60 minutes. /8

According to one of the main features of the invention and due to the fact that by properly selecting the vulcanizing agent or agents the length of the -R- group can be established as desired, one gets vulcanized elastomers presenting characteristics of rigidity and flexibility that can be determined a priori; as a matter of fact, by using vulcanizing compounds according to the invention in which the length of the -R- group is reduced, for example, succinic or glutaric acid or tetramethylenediamine, one gets a vulcanized product where the polymeric chains of the elastomer are linked by transversal elements with a reduced length and, consequently, the vulcanized elastomer will have a certain rigidity. Vice versa, using vulcanizing compounds according to the invention where the length of the -R- group is greater, for example, sebacic acid, one will get a vulcanized product where the polymeric chains of the elastomer are linked by transversal elements with a greater length, which leave the polymeric chains linked together relatively free to move with respect to each other, providing a vulcanized elastomeric product that will offer high flexibility.

According to the invention, it is furthermore possible to influence the viscoelastic characteristics of the vulcanized product not normally by way of the proper choice of the chemical nature (R is arylene, then the steric size of the transversal chains will be quite different from the size that can be obtained where R would be, vice versa, alkylene, with the /9 obvious consequences regarding the viscoelastic characteristics of the final vulcanized product) and the length of the -R- group, but also through the choice of the degree of epoxidation of the epoxidized elastomer that is a part of the starting mixture through an opportune stoichiometric dosage of the vulcanizing agent or agents and finally through the use, in combination, of vulcanizing agents having different -R- groups and possibly also different functional R₁ and R₂ groups. One therefore gets a very high degree of operative flexibility, which makes it possible easily during the production phase to adjust the characteristics of the vulcanized product to the requirements.

Where R₁ and R₂ are carboxyl, one gets cross-links between the elastomeric chains that are of the exclusively polyester type according to diagram (A). According to a further feature of the invention, one can arrive at the same results by means of a mixture where the vulcanizing agent would be one of the elastomers of the mixture itself, properly functionalized by

means of lateral carboxylic groups. In this case, one also starts with an elastomer that is epoxidized to a predetermined degree, ENR 25 or 50, and with it one prepares a mixture, mixing it with possible charges, for example, carbon black, or with another elastomer, where the repetitive units of the polymeric chain present at least one carboxylic group, for example, /10 defined by a butadiene-acrylic acid copolymer such as the product that is available under the name of KRYNAC (registered trademark) and that is distributed by POLYSAR of the BAYER Group, which precisely is a butadiene-acrylic acid copolymer with 30% by mole of acrylic acid. During the next vulcanization phase, which takes place in the same manner as described before, one now gets a lateral link between the ENR chain and the KRYNAC chain with formation of esteric bridges according to the following diagram:



The resultant vulcanized product therefore, although it does not have the characteristic of presenting a controllable

flexibility on the basis of a proper choice of the length of the lateral chains (the latter, as a matter of fact, according to the reaction diagram (D) all have equal length), however, presents the feature of not being toxic, such as the products obtainable from the mixture of ENR and bi- or polycarboxylic acids.

On the basis of the above, both these latter mixtures and those where in the place of the organic acids one uses diamines or bisulfonate molecules or those on a base of ENR-KRYNAC can therefore be defined as "self-vulcanizing" or "self-reticulating" mixtures since, when placed under conditions of vulcanization, they give rise to the formation of cross-links between the elastomer chains without which one would need the presence of sulfur and the traditional accelerators on a sulfuric base or peroxides. This definition is particularly indicated by the mixture on the base of epoxidized elastomers and elastomers provided with carboxylic groups in the repetitive units: On the other hand, as a matter of fact, strictly speaking, in the case of mixtures of epoxidized elastomer and compounds according to formula (1), the latter can be viewed as new specific vulcanizing agents to be used as an alternative to sulfur or peroxides where the addition reaction upon the epoxidic ring with the formation of esters takes place directly among the elastomers, whereas among those of them that are

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different, the starting mixture turns out to contain, apart from any possible charges, only elastomers, and it is therefore, properly speaking, self-vulcanizing.

The invention will now be described with reference to some exemplary embodiments.

EXAMPLE 1 - High hardness formula.

Operating with open, 14x16-inch, two-wheel mixer, one prepares for a period of 6 minutes a mixture having the following composition:

ENR-25 (EPOXYPRENE 25™)	100 phr
Carbon black (N326)	80 phr
Citric acid.	20 phr
Terephthalic acid.	5 phr

The 25% by mole epoxidized polymer (ENR-25) is supplied by MRPRA (Malaysian Rubber Producers' Research Association). The mixture is then put under pressure at 160°C for 20 minutes and the resultant vulcanized product is subjected to mechanical tests (traction rupture, resilience, hardness) and the traditional flowmeter tests operating according to the ASTM D2240, D2632, D2048, D412 standards. Here are the results obtained:

Mechanical tests:

Module, 50% elongation.	12.50 MPa
Elongation upon rupture.	52.9%
Load upon rupture.	13.50 MPa
Hardness (Shore-A).	95
Hardness (Shore-D).	50
- Resilience (Monsanto MDR 2000E flowmeter) at 160°C:	
ML (minimum module).	7.82 dN.m
MH (maximum module).	56.87 dN.m
T10 (time at 10% pair).	0.23 minute
T50 (time at 50% pair).	1.09 minute
T90 (time at 90% pair).	4.19 minutes
- TAN delta (damping).	0.017

EXAMPLE 2 - Medium hardness formula.

Operating as in Example 1, one prepares a mixture having the following composition:

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ENR-25 (EPOXYPRENE 25™).	90 phr
Chlorinated butyl rubber.	10 phr
Carbon black (N660).	80 phr
Citric acid.	2.5 phr
Sebacic acid.	5.0 phr
Zinc oxide.	0.6 phr

The mixture is then placed under pressure at 170°C for 60 minutes and the resultant vulcanized product is subjected to

tests according to ASTM D2240, D2632, D2048, D412. Here are the results obtained:

- Mechanical tests:

Module, 10% elongation.	0.64 MPa
Module, 25% elongation.	1.57 MPa
Module, 50% elongation.	3.52 MPa
Elongation upon rupture.	89.4%
Load upon rupture.	7.83 MPa
Hardness (Shore-A).	78

- FIRESTONE Flexometer (heat generation):

Final temperature.	84°C
Deflection prior to test.	7.1 mm
Deflection after test.	10.3 mm
- TAN delta (damping).	0.663 (at -20°C)
	0.705 (at 0°C)
	0.690 (at +60°C)

EXAMPLE 3 - Low hardness formula.

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Operating as in Example 1, one prepares a mixture having the following composition:

ENR-25 (EPOXYPRENE 25™).	100 phr
Carbon black (N660).	50 phr
Maleic acid.	1.5 phr
Citric acid.	1.5 phr

The mixture is then placed under pressure at 170°C for 60 minutes and the resultant vulcanized product is subjected to tests according to ASTM D2240, D2632, D2048, D412. Here are the results obtained:

- Monsanto MDR2000E flowmeter (done at 193°C):

ML	1.19
MH	12.02
T10	0.50
T50	6.22
T90	34.50

- Mechanical tests:

Module, 10% elongation.	0.32 MPa
Module, 25% elongation.	0.73 MPa
Module, 50% elongation.	1.31 MPa
Module with 100% elongation.	2.92 MPa
Module with 150% elongation.	5.25 MPa
Module with 200% elongation.	8.01 MPa /15
Elongation upon rupture.	200%

Load upon rupture.	8.01 MPa
Hardness (Shore-A).	63

- FIRESTONE Flexometer (heat generation):

Final temperature.	98°C
Deflection prior to test.	13.7 mm
Deflection after test.	16.1 mm

- TAN delta (damping) 0.231 (at +30°C)

EXAMPLE 4

Operating as in Example 1, mixtures labeled A to D were prepared with the composition listed in Table 1. Subsequently, the mixtures were placed under pressure at 160°C for 45 minutes. Finally, the vulcanized product, thus obtained, was subjected to tests according to ASTM D2240, D2048, D2632, D412, repeating the mechanical extension test on only vulcanized samples and on vulcanized samples that were also aged by keeping them in air for three days at 70°C. The results are shown in Table 1.

TABLE 1

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TABELLA 1

Composizione	A	B
(phr)		
ENR-25	100,0	100,0
nero fumo N339	50,0	40,0
a. tereftalico	10,0	
a. adipico		1,7
a. fumarico	5,0	
a. sebacico		6,6
ML	1,9	1,0
Reometro	63,0	43,1
a 193°C	T10	0,53
Monsanto	T50	3,44
MDR2000E	T90	18,03
CR	11,10	13,60
Prova	25%	3,48
traz.	50%	6,40
(non	100%	12,1
inv.)	AR	81
		110
CR		12,00
Prova	25%	2,48
traz.	50%	4,87
(inv.)	100%	12,00
	AR	101
Shore A	86	80

CR = rupture load; AR = rupture extension.

[Key: 1) Composition; 2) Carbon black; 3) Terephthalic acid; 4) Adipic acid; 5) Fumaric acid; 6) Sebacic acid; 7) Flowmeter; 8) At; 9) Traction test; 10) Not aged; 11) Aged].

EXAMPLE 5

Operating as in Example 1, one prepares a mixture having the following composition:

ENR-50 (EPOXYPRENE 50TM) 50 phr

KRYNAC (a functionalized elastomer with carboxylic groups
consisting of a butadiene-acrylic acid copolymer, 30% by mole of
acrylic acid) is distributed by POLYSAR (BAYER). The mixture is

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then pressurized at 150°C for 45 minutes and the resultant vulcanized product is subjected to tests according to ASTM D2240, D2632, D2048, D412, repeating the mechanical extension test on only vulcanized samples or those that were hot-treated under pressure) and vulcanized and aged samples by keeping them in air for three days at 70°C. Here are the results:

- Monsanto MDR2000E flowmeter at 193°C:

ML 1.15

MH 16.50

T10 0.51

T50 4.47

T90 19.57

Traction tests (comparative data on vulcanized material):

	Normal	Aged
Module at 10%	0.51 MPa	0.59 MPa
Module at 25%	0.86 MPa	0.98 MPa
Module at 50%	1.61 MPa	2.01 MPa
Module at 100%	2.88 MPa	4.23 MPa
Module at 200%	7.83 MPa	-
Rupture extension	227%	177%
Load upon rupture	9.56 MPa	10.2 MPa
Hardness (Shore-A)	72	
Rebound resilience		15%

- FIRESTONE Flexometer (on vulcanized material):

EXAMPLE 6

Operating as in Example 1, but in a closed mixer (of the Brabender plasticorder type), one prepares a mixture having the following composition:

NEOPRENE (polychloroprene) 50 phr

The mixture presents the following flowmeter characterization:

- Monsanto MDR2000E flowmeter at 193°C:

ML	0.70
MH	6.12
T10	1.20
T50	7.56
T90	21.40

One also prepares two "white" mixtures, one on a base only of epoxidized natural rubber (EPOXYPRENE-50) and the other one only on a base of KRYNAC 221. Both of these mixtures show an absence of vulcanization in the flowmeter test (MH-ML=0).

CLAIMS

1. Procedure for vulcanization without sulfur of elastomers, characterized in that it comprises the following phases:

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- preparation of a mixture including at least one elastomer epoxidized to a predetermined degree and a predetermined quantity of at least one compound having the following formula:

R1 - R - R2

where R is arylene, alkylene, alkenylene, substituted or not substituted, or a mixture of same and where R1 and R2 are

indifferently a carboxylic group, an aminic group and a sulfonic group or chlorosulfonic group; and

- subsequently, hot and under pressure, treating the mixture thus prepared.

2. Process according to Claim 1, characterized in that said mixture is treated under pressure at a temperature of between 130 and 180°C for a period of time between 20 and 60 minutes so as to obtain the complete chemical addition reaction for said R1 and R2 groups on the epoxidic rings of the epoxidized elastomer.

3. Process according to any of the above claims, characterized in that said mixture contains a plurality of diverse chemical compounds mixed together and all in accordance with the general formula R1-R-R2 where R, R1 and R2 are as defined in Claim 1; the total quantity in terms of weight related to the total weight of the epoxidized elastomer of said chemical compounds is between 0.1 and 30 parts by weight for every 100 parts by weight of epoxidized elastomer.

4. Process according to any of the above claims, characterized in that said mixture is prepared by mixing an elastomer epoxidized to a degree of between 20 and 50% by mole with a bi- or polycarboxylic acid chosen in the group made up of oxalic, malonic, succinic, glutaric, adipic, sebacic, maleic, fumaric, phthalic, isophthalic, terephthalic, citric acids or a mixture of two or more of same.

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5. Process according to Claim 4, characterized in that for the preparation of said mixture, one uses at least one bi- or polycarboxylic acid having a pK_a of between 0.5 and 5.5 to act as accelerator.

6. Self-vulcanizing mixture containing at least one elastomer epoxidized to a predetermined degree, characterized in that it comprises a predetermined percentage of one or several vulcanizing agents having the following formula:



where R is arylene, alkylene, alkenylene, substituted or not substituted, or a mixture of same, and where R₁ and R₂ are indifferently a carboxylic group, an aminic group and a sulfonic group or chlorosulfonic group.

7. Mixture according to Claim 6, characterized in that it contains between 0.1 and 30 parts by weight for every 100 parts of epoxidized elastomer of a bi- or polycarboxylic acid chosen from among the group made up of: oxalic, malonic, succinic, glutaric, adipic, sebacic, maleic, fumaric, phthalic, isophthalic, terephthalic, citric acids; or a mixture of same.

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8. Mixture according to Claim 7, characterized in that it comprises a mixture of at least two of said bi- or polycarboxylic acids where one of said acids has a high pK .

9. Mixture according to Claim 6, characterized in that it comprises a predetermined percentage of a diamine.

10. Self-vulcanizing mixture containing at least one elastomer epoxidized to a predetermined degree, characterized in that it comprises a predetermined quantity of a second elastomer where the repetitive units of the polymeric chain present at least one carboxylic group.

11. Mixture according to Claim 10, characterized in that it comprises at least one epoxidized elastomer and at least one butadiene-acrylic acid copolymer.

12. Mixture according to Claim 11, characterized in that said butadiene-acrylic acid copolymer consists of 30% by mole of acrylic acid and in that said epoxidized elastomer is ENR with 25 to 50% by mole of epoxidation.

13. Mixture according to one of Claims 10 to 12, characterized in that it furthermore comprises polychloroprene.

p.1.: FIRESTONE INTERNATIONAL DEVELOPMENT S.p.A.

Plebani Rinaldo

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